Wood-Based Biorefinery
Value Added Co-Products
From Woody Biomass to Chemicals and Energy

Thomas Amidon and Shijie Liu and thanks to Dr. Art Stipanovic
Department of Paper and Bioprocess Engineering
&
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Outline

- Overview
- Fractionation Products
- Fractionation uses
- Alkaline Pulping, Fiber/Wood Quality
- Wood Products Applications?
- Application in New York
Overview: Renewable – “Catch and Release”

From Woody Biomass to Chemicals and Energy
Overview - Add Wood Products Box

Plant Biomass

- Volatile Extractives
- Lignin
- Hemicelluloses
- Cellulose

Chemicals

Energy

Ethanol

Biodegradable Plastics

Paper
Overview: Wood

Inorganic Components
K & Ca (400 ~ 1000 ppm);
Mg & P (100 ~ 400 ppm); and 70 others

Extractives
Aliphatic and alicyclic: Terpenes; terpenoids; esters;
fatty acids; alcohols; …
Phenolic: phenols; stilbenes; lignans; isoflavones; …
Others: sugars; cyclitols; tropolones; amino acids, …

Hemicelluloses

Cellulose and Lignin
Biorefinery Product Overview

- Extraction (prior to Pulping or Burning)
- Fractionation of Wood Extracts – Sugars, Lignin, Methanol, Furfural, Acetic Acid
- Fermentation (for sugars and minor)
- Purification – Ethanol/PHA/Lactic Acid/Butanol/Butane diol etc.
- Pulping/Papermaking, pellets, chipboard, flake/strandboard, fiberboard
- Burning/Gasification for Power or FT
Fractionation Products

- Acetic Acid
- Acetates
- Hexoses, Pentoses
- Oligomers
- Lignin fragments
- Furfurals
- Wood chips (Changed)
Ethanol Fermentation

- Micro-organisms
  - Natural Strains: *Candida* Shehatae, *Yamadazyma* Stipitis, etc.
  - Recombinant Strains: *E*-Coli, *S*. *Cerevisiae*

- Anaerobic vs. Aerobic
  - Cell growth
  - By-products

- Other fuel chemicals
  - Hydrogen; Butanol; Propanol; …
Alkaline Pulping

- Extraction & Hemicelluloses removal
  - Uronic acid
  - Acetyl groups
  - Carboxyl groups
  - Metal ions

- Lignin
  - Lignin-hemicellulose bonds
  - Active chemical agent access to lignin sites
Alkaline Pulping & Fiber/Wood Quality

- Mild cooking / bleaching conditions
- Sulfur-free if desired, TCF?
- Low Acetyl, higher lignin and cellulose
- Low Hemicelluloses content
  - High Freeness for the same other indices
  - High SEC to reduce freeness/ Bulky sheet
- Fiber-Fiber bonding concerns
- Higher Cal./Kg. wood chips
- Paper Industry - Cellulose for Paper and Lignin for Energy yields low profitability
- Insert a new process in front of the digester to extract hemicellulose and convert to ethanol, PHA's etc. recover acetic acid and enhance energy efficiency
- Estimated Profit increase for complete Paper Industry application is $3.3 Billion per year (Thorp - PIMA '04 Presentation)
- Total estimated at 1.9 Billion gallons ethanol and 600 Million gallons acetic acid for industry wide application
• Wood burning industry - low cost wood needed to be economic

• Evolutionary Change Example - Wood cost at $40 per dry ton ($0.02/dry pound) and extraction at 15% of mass recovered: 2/3 sugars 1/3 acetic acid/extractives

• Sugars valued at $0.07/pound and acetic acid/extractives at $0.30/pound Ave. $0.146/lb. value for the 300 pounds recovered value equal to all of the wood cost

• Residue burned with cost reduction greater than the ~20% of mass lost

• Biomass Willow an economic fuel crop
Process Effects on Potential Wood Products - Uses for Extracted Wood

- Need comminution to extract – Chips, flakes, strands, or fiberized – OK
- Extracted wood – Lower density 15-25%, most hygroscopic hemi’s removed
- Chip dimensions not appreciably changed.
- Some darkening
Intermediate Conclusions

- Autocatalytic Water Extraction of Hemi
- Milder Cooking and Bleaching Requirements
- Freer and Bulkier Pulp
- Improved Burning residue for energy use
- “Lower moisture reactivity of wood products?”
Cellulose Utilization

- Whole Wood Fibers: Paper
- Fiber Crystallites: “Lite” Composites and SRM’s
- Cellulose $\rightarrow$ Glucose $\rightarrow$ Ethanol
- Glucose $\rightarrow$ Levulinic Acid
Preparation of Cellulose "Nano" crystals

Treatment with Acid plus Mechanical Shearing
12-65% H₂SO₄, 40-100°C, 1-3 hours (W.T. Winter et. al)
Magnetic Cellulose Fibers: Lumen Loaded with Fe$_3$O$_4$ : < 5 micron Particle Size
Biofine Levulinic Acid Process
2 Stages: Cellulose -> Glucose -> LA

- Dilute Aqueous $\text{H}_2\text{SO}_4$ at Elevated Temperatures. 2 Reactors
- Conversion Time: 25 minutes vs. hours / days for enzymatic processes
- Continuous, Reasonable Yield (40-50% based on dry cellulose)
- Byproducts: formic acid, furfural and a high BTU char
Levulinic Acid (LA)

- A.K.A: 4-oxopentanoic acid, 4-ketovaleric acid
- Current Market: 2 MM pounds/year at $3.50/lb
- Derived from Maleic Anhydride (petroleum based)
- Estimated Cellulose based Cost: 1/3-1/8 oil base
Levulinic Acid & Derivatives

- Succinic Acid
- Diphenolic Acid
- Monomers
- Industrial Solvents
- Epoxy resins/coatings

CELLULOSE

2-Methyltetrahydrofuran

5-Aminolevulinic Acid

MTHF  DALA

From Woody Biomass to Chemicals and Energy
Levuulinic Acid as a “Biodiesel” Fuel and home heating Oil
LA in diesel fuel/heating oil provides poor miscibility
LA Esterified with Ethyl Alcohol Yields Ethyl Levulinate (ELA)
79% diesel + 20% ELA + 1% isoamyl alcohol *meets ASTM D975 standard* for diesel fuel (low S !)
Production of Biodegradable Plastics

- Most consumer plastics are petroleum based and are not biodegradable.
- 20-25% of the US landfill volume is plastic although trash is only 7% plastic
- 62% of trash found on beaches is plastic
- “Biodegradable” plastics are a very helpful development for many uses
Biodegradable Materials from Woody Biomass

Certain Bacteria Can Utilize Hemicellulose sugars and LA to Produce Intracellular Polyesters (Nakas, Keenan at ESF).

These polyesters are “thermoplastic” (Heat ‘em up they melt)

Thermoplastics are useful for disposable consumer items

Such polyesters are biodegradable (Good News for Landfills, etc.)
Applications for Hemicellulose

- Polymer composites and blends
- Fibers from liquid crystalline phases (co-extrusion with cellulose)
- Acetic Acid Separation
- Conversion from xylose:
  - Bioplastics (with levulinic acid)
  - Ethanol and organic acids
  - Furfural and furan polymers
  - Xylitol and 2,3 butanediol
Progress in Lignin Utilization

- Fungal biodelignification and / or ligninase enzymes
- Water Extracted Lignin
- Oxygen / Alkali “Sulfur-Free” pulping to separate lignin.

Applications for Sulfur-Free Lignin:
- Adhesives and Plastics
- Biodispersants / Emulsifiers
- Cosmetics and Pharmaceuticals
- Cattle Feed
Product Evolution Where is it going?

Paper Industry – Cellulose for Paper and Lignin for Energy with Hemicellulose and extractable for New Materials

Wood burning industry – Lignin as Fuel and all other components for New Materials

Wood Products industry – extracted wood for reconstituted wood products and composites?

Purpose-built Biorefinery – All components available for New Materials

- Technology will differ for each industry
- Waste and energy recovery
  - Gasification and FT evolution has begun
Key Gaps

- Smart Integration – Energy, Water, Wood
- Extraction – Pulp/Wood Property impacts
- Separation – Cost/energy reduction
- Conversion – Lower cost Ethanol, Butanol PHAs etc. – Higher value products
- Business model and financing - I think it is viable now – Hardwoods for pulp tissue/fluff/stiffness and hog fuel/electricity
- Wood Products Property Marketing
Broader Factors to Consider

- Vision for the Forest Products Business
- Green Power incentives/ Portable fuel
- Non-Sulfur gasification
- Carbon credits
- Sustainable society
MY Conclusions

- Biorefinery: a strategic direction to Energy Materials and Chemicals
- ESF Biorefinery: water-based technology, Hwd application advantage
- Essential components: Extraction; Fractionation; Fermentation; Pulping; Bleaching; Papermaking; Reconstituted Wood Products: Or Burn/Gasify
.... forests can be made to produce fifty times their present volume of end products and still remain a permanently self-renewing source for raw materials......

Only forests - no other raw material resource - can yield such returns. The forest can, and so must, end the chronic scarcities of material goods that have harassed man’s experience since the beginning of history.
ESF Biorefinery Initiative

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Hemicellulloses

- **Hardwood:**
  - Glucomannan
  - Glucuronoxyylan (Xylan)

- **Softwood:**
  - Galactoglucomannan
  - Arabinoglucuronoxyylan (Xylan)
Hemicelluloses

- **Hexoses (6-carbon sugars: C\(_6\)H\(_{12}\)O\(_6\))**
  - D-glucose; D-mannose; D-galactose

- **Pentoses (5-carbon sugars: C\(_5\)H\(_{10}\)O\(_5\))**
  - D-xylose; L-arabinose; D-arabinose

- **Hexuronic Acids (C\(_7\)H\(_{12}\)O\(_7\), C\(_6\)H\(_{10}\)O\(_7\))**
  - 4-O-methyl-D-glucuronic acid; D-galacturonic acid; D-glucuronic acid

- **Deoxyhexoses (C\(_6\)H\(_{12}\)O\(_5\))**
  - L-rhamnose (6-deoxy-L-mannose);
  - L-fucose (6-deoxy-L-galactose)
Hot-Water Extraction

- Abundant
- Safety, Environmental, Reuse
- Catalyst Use
- Product Value Preservation
- Product Separation Ease
- Membrane technology
How

- Hardwoods are advantaged
- Use water as the solvent
- Use Membrane/Filtration Technology
- Commercialize pentose fermentations
- Use conventional wood chips and preserve structure in process